by one-electron outer-sphere quenchers should be of interest.

Conclusions

Luminescence quenching of $Ru(bpy)_3^{2+*}$ by $S_2O_8^{2-}$ in aqueous and mixed acetonitrile–wate solutions occurs by both unimolecular and bimolecular pathways. The nondiffusional pathway results from the ground-state association of $Ru(bpy)_3^{2+}$ with $S_2O_8^{2-}$. The lifetime of the photoexcited ion pair is shorter than $Ru(bpy)_3^{2+*}$ in all solvent combinations investigated but long enough to allow the excited complex to be quenched by a second $S_2O_8^{2-}$ as well as luminescence at the characteristic emission wavlengths of $Ru(bpy)_3^{2+*}$. An unusually strong dependence of bimolecular and unimolecular quenching rates on the solvent employed suggests that both quenching reactions occur by electron transfer and that the rate-limiting step in both mechanisms is solvent reorganization of one or both reactants.

The analysis of steady-state luminescence and lifetime measurements demonstrates that coincidence of I^0/I and τ^0/τ values is expected for the general case of ground-state ion pairing provided that the lifetime of the excited ion pair is relatively long.

Acknowledgment. This research was supported by the Army Research Office (DAAG 29-82-K-0006) and the National Science Foundation (CH7903729). The experiments and analysis of data from laser flash experiments were performed at the Center for Fast Kinetics Research (CFKR) at The University of Texas at Austin. The CFKR is supported jointly by the Biotechnology Branch of the Division of Research Resources of NIH (RR00886) and the University of Texas at Austin.

Registry No. $Ru(bpy)_3^{2+}$, 15158-62-0; $S_2O_8^{2-}$, 15092-81-6; CH_3CN, 75-05-8; H_2O, 7732-18-5; $(NH_4)_2SO_4$, 7783-20-2; $K_4Fe(CN)_6$, 13943-58-3.

A Comparative Rate Method for the Study of Unimolecular Falloff Behavior

Walter Braun, J. R. McNesby,† and Milton D. Scheer*

Center for Chemical Physics, National Bureau of Standards, Washington, D.C. 20234
(Received: June 7, 1983)

A comparative method was applied to a high-temperature fast-flow reactor to determine relative kinetic parameters for the two-channel decomposition of cyclobutanone in the falloff region. The applicability of this method to such nonthermally equilibrated systems was assessed and found to be generally useful over a wide range of conditions. The measurements could, therefore, be used as a quantitative diagnostic tool for sensing unimolecular falloff behavior in a number of heat bath gases. A simple stepladder collisional activation–deactivation model was used to determine the energy transferred per collision. The values obtained for the heat bath gases He, Ar, SiF_4, and SF_6 were 3.0, 2.0, 3.5, and 4.0 kcal/mol, respectively. These are small multiples of RT and very small fractions of the activation energy, indicating that weak collisions must be a dominant feature of reaction types represented by the decomposition of cyclobutanone.

Introduction

Energy transfer models applicable to unimolecular dissociation processes have been assessed and a considerable body of literature exists on the subject.[14] Still, it is not yet entirely certain how the average energy transferred per collision varies with the energy content of the decomposing molecule and the temperature of the bath gas. Although direct methods for assessing the energy transferred per collision have recently been described,[2] the usual approach, and the one which we adopt, involves (1) measuring decomposition rate constants for various pressures of the heat bath gas, (2) computing $k(E)$ vs. energy, (3) applying these energy-dependent rates to the energy level populations calculated by means of an appropriate energy transfer model, and (4) comparing the macroscopic rate constants obtained from these calculations with the experimental results.

A typical energy transfer model involves a single parameter, namely, the average energy transferred either up or down an energy ladder with constant spacing. The energy dependences of the probability of such energy transfers that have been used previously[1] are the Dirac Δ function or stepladder, the exponential function, and the Poisson and Gaussian functions. The general feature of these models are quite similar, and experimental results have not definitively distinguished between them. The comparative experimental method of evaluating kinetic parameters has been successfully applied at high pressures to fully thermalized unimolecular systems in single-pulse shock tubes by Tsang.[5] We have adapted his method to a study of the kinetics of flowing reactive systems at much lower pressures. The method compares the ratio of decomposition rates of two simultaneously occurring reactions and is insensitive to temperature inhomogeneities (see Appendix). The measurements that we will describe complement those made at much lower pressures by the so-called "very low-pressure pyrolysis" (VLPP) method.[6-8] The VLPP measurements are taken with decomposition occurring where the activated reactant energies are very close to E_0, the threshold energy, while at higher pressures progressively higher energy levels become involved. The measurements described here for heated flow systems can also be compared with infrared laser heating.[9-13]

---

† Chemistry Department, University of Maryland, College Park, MD 20742.

(1) D. C. Tardy and B. S. Rabinovitch, *J. Chem. Phys.* **45**, 3720 (1966); D. C. Tardy and B. S. Rabinovitch, *Chem. Rev.*, **77**, 369 (1977).

(2) J. R. Barker, M. J. Rossi, and J. R. Pladziewicz, Abstracts of papers presented at the "7th International Symposium on Gas Kinetic", University of Gottingen, Gottingen, Germany, 1982; H. Hippler, J. Troe, and H. J. Wendelken, *Ibid.*

(3) R. C. Bhattacharjee and W. Forst, *Chem. Phys.*, **30**, 217 (1978); **37**, 343 (1979).

(4) N. Snider, *J. Chem. Phys.*, **78**, 6030 (1983).

(5) See, for example, (a) W. Tsang, *Int. J. Chem. Kinet.*, **10**, 599 (1978); (b) W. Tsang, in "Shock Waves in Chemistry", Lifshitz, Ed., Marcel Dekker, New York, 1981, Chapter 2.

(6) D. M. Golden, G. N. Spokes, and S. W. Benson, *Angew. Chem., Int. Ed., Engl.*, **12**, 534 (1973).

(7) R. B. Gilbert and K. D. King, *Chem. Phys.*, **49**, 367 (1980).

(8) K. D. King, T. T. Nguyen, and R. G. Gilbert, *Chem. Phys.*, **61**, 221 (1981).

(9) W. Braun, M. J. Kurylo, and A. Kaldor, *Chem. Phys. Lett.*, **28**, 440 (1974).

(10) W. Shaub and H. S. Bauer, *Int. J. Chem. Kinet.*, **7**, 509 (1975).

(11) V. Starov, N. Selamogh, and C. Steel, *J. Am. Chem. Soc.*, **103**, 7276 (1981).

(12) D. F. McMillan, K. E. Lewis, G. P. Smith, and D. M. Golden, *J. Phys. Chem.*, **86**, 709 (1982).

(13) M. D. Scheer, J. R. McNesby, and W. Braun, following paper in this issue.

0022-3654/84/2088-1846$01.50/0 © 1984 American Chemical Society

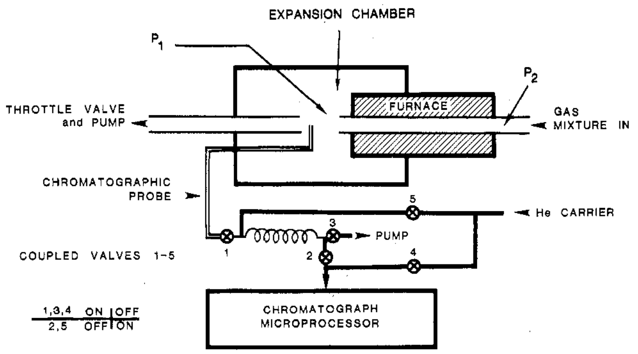

Figure 1. Schematic diagram of the experimental apparatus.

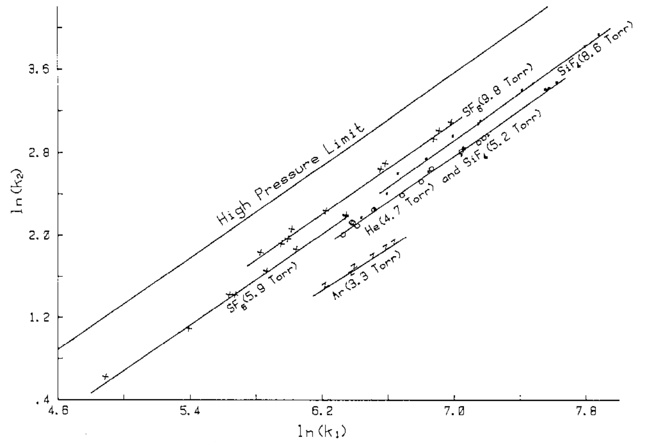

Figure 2. Comparative plots of the experimental data for the two-channel decomposition of cyclobutanone in Ar (3.3 torr), He (4.7 torr), SiF_4 (5.2 and 8.6 torr), and SF_6 (5.9 and 9.8 torr) heat bath gases.

In the present work we explore the application of the comparative method to unimolecular reactions in the falloff region. It will be shown that this method, while based upon an Arrhenius description with the implicit assumption of a vibrational Boltzmann equilibrium in the reactant, still yields important information for the non-Boltzmann distributions that are characteristic of unimolecular dissociation in the falloff region. The information so obtained is then compared with the rate constants calculated by means of a stepladder energy transfer model.

The Comparative Method

The two channels involved in the decomposition of cyclobutanone are

$$\text{cyclobutanone} \xrightarrow{k_1} C_2H_4 + CH_2CO$$
$$\xrightarrow{k_2} c\text{-}C_3H_6 + CO$$

The amounts of ethylene (X_1) and cyclopropane (X_2) formed during the reaction time τ are given by

$$X_1 = R_0(k_1/(k_1 + k_2))(1 - \exp(-(k_1 + k_2)\tau)) \quad (1)$$

$$X_2 = R_0(k_2/(k_1 + k_2))(1 - \exp(-(k_1 + k_2)\tau)) \quad (2)$$

where R_0 is the initial concentration of cyclobutanone and k_1 and k_2 are the rate constants for each of the two channels. The Arrhenius expressions $k_1 = A_1 \exp(-E_1/RT)$ and $k_2 = A_2 \exp(-E_2/RT)$ are thought to be applicable only when the reactant is thermally equilibrated with a suitable heat bath gas. Under these conditions it is readily shown that

$$\ln (k_2) = (E_2/E_1) \ln (k_1) - (E_2/E_1) \ln (A_1) + \ln (A_2) \quad (3)$$

where $k_1 = Z/\tau(1 + (X_2/X_1))$, $k_2 = Z/\tau(1 + (X_1/X_2))$ and $Z = -\ln (1 - ((X_1 + X_2)/R_0))$. In examining the dependence of ln (k_2) upon ln (k_1), one is in effect plotting ln (k_1) and ln (k_2) vs. $1/T$ in the three-dimensional space defined by the orthogonal axes ln (k_1), ln (k_2), and $1/T$. This results in two planes that intersect in a line whose projection onto the ln (k_1)–ln (k_2) plane comprises the comparative methodology. Since the effect of the projection operation is to eliminate temperature as a variable it becomes clear why temperature inhomogeneities do not significantly influence either the slope or intercept of eq 3 as long as both reactions undergo identical temperature–time histories. Sources of uncertainty obviously arise if the Arrhenius expression is not an adequate description of the rate constant dependence upon temperature. It will be shown that, when both reactions are in the falloff region, the plot of ln (k_2) vs. ln (k_1) maintains its linearity. Variations in the intercept of such comparative plots are far more sensitive to unimolecular falloff than are changes in the slope.

Experimental Section

Figure 1 shows the components of the apparatus employed in this investigation. It is extremely difficult to construct a furnace that does not have some axial and transverse temperature gradients and no serious attempt has been made to eliminate them. As stated above we avoid the ambiguities assoicated with such temperature nonuniformities by using the comparative rate method. The method, however, does entail some uncertainty in the reaction time which will be discussed in greater detail below. Apparatus parameters are as follows: (1) The heated reactor consists of a 5 mm i.d. 10 cm long quartz tube. (2) The gas flow through the heated tube is fast with a residence time that is less than 3 ms. (3) The furnace temperature is fully adjustable up to about 1200 K. The temperature profile in the reactor was determined with a thermocouple probe that could be axially positioned at any point along the reactor tube. The flowing gas tends to cool the reactor tube so that the experimentally useful range of pressure was found to be between 1 and 10 torr where the lower limit is determined by the requirement that the rate of molecular collisions greatly exceeds those made with the tube wall. Sample mixtures were prepared in 10-L bulbs, with 1–5 mol % of reactant with either He, Ar, SF_6, or SiF_4 as heat bath gases. A small, accurately known quantity of inert methane was added to each mixture so that fractional conversions could be determined without analyzing for the residual reactant concentration. The chromatographic column used was Poropak P and a flame ionization detector was employed to measure hydrocarbon products. The fractional conversion reproducibility was ±2%. The gas leaving the reactor tube expands and cools so that further decomposition is quenched. About 10% of the flowing gas is sampled by expansion into a cooled evacuated sampling loop after the flow becomes steady. The sampling loop is then isolated; its contents are pressurized to 1 atm with helium and a representative sample is injected into the gas chromatograph. At a total pressure of 1 torr with a 100:1 ratio of heat bath gas to reactant, 1% decomposition produces a chromatographic signal-to-noise ratio of about 10:1 for products that are eluted during the first 10 min.

The steady-state gas pressure in the furnace tube is constant but experiences a large pressure drop at the exit. The pressure in the reactor was monitored with a capacitance pressure gauge at P_1 and P_2 in Figure 1 and volume rates of flow were measured for all of the heat bath gases as a function of the pressure (P_1) in the expansion section. These rates of flow were shown to be rapid enough so that the tube exit exhibited the properties of a critical orifice. Under such circumstances the pressure in the furnace tube is approximately constant and is close to P_2, the upstream pressure. Reaction times in the hot tube were calculated from this pressure and the flow measurements. The major uncertainty in this calculation resides in an estimate of the effective length of the reaction region in the heated tube. The previously mentional thermocouple measurements indicate the temperatures that each unit of flowing gas encounters along the tube axis for times determined by the flow velocity. The method by which this effective length is calculated is given in the Appendix.

Results

1. Experimental Measurements. Figure 2 displays all of the experimental results for the cyclobutanone decomposition plotted in accordance with eq 3. The least-squares lines all have a slope of 1.11 within one standard deviation of 0.04. The limiting

TABLE I: Calculated Specific Rate Constants for the Dissociation of Cyclobutanone into Product Channels 1 and 2 Respectively as a Function of Energy

energy/ (kcal/mol)	k_1/s^{-1}	k_2/s^{-1}
46.00	0.00	0.00
51.00	8.19×10^2	0.00
56.00	6.84×10^4	0.00
61.00	8.72×10^5	5.17×10^3
66.00	5.17×10^6	8.95×10^4
71.00	2.10×10^7	6.47×10^5
76.00	6.61×10^7	2.98×10^6
81.00	1.74×10^8	2.98×10^7
86.00	4.01×10^8	5.03×10^7
91.00	8.31×10^8	7.37×10^7
96.00	1.58×10^9	1.63×10^8
101.00	2.81×10^9	3.27×10^8
106.00	4.73×10^9	6.12×10^8
111.00	7.58×10^9	1.07×10^9
116.00	1.17×10^{10}	1.80×10^9
121.00	1.73×10^{10}	2.87×10^9
126.00	2.48×10^{10}	4.41×10^9
131.00	3.47×10^{10}	6.54×10^9

high-pressure line is shown for comparison.[14,15] It is evident that the rate parameters are not at their high-pressure limiting values and that the effectiveness of the heat bath molecules in approaching the limit is in the order $SF_6 > SiF_4 >$ He > Ar. Even though the experimental lines are significantly displaced from the high-pressure limit, the slopes are remarkably constant and in fact cannot be distinguished from the high-pressure value of 1.114. In order to understand why this is so it is necessary to relate the collisional activation–deactivation efficiencies to an average energy transferred per collision. This depends in turn upon the details of the model used to describe the energy transfer process. Once we have a numerical simulation of the rate constant as a function of temperature and pressure we can make a separate assessment of the suitability of the Arrhenius equation and hence the applicability of such comparative plots to nonthermalized vibrational distributions.

2. *Energy Transfer Model: Calculation of Rate Constants.* The simple stepladder model has been shown by Rabinovitch and co-workers[1] to give results that are qualitatively similar to those of other energy transfer probability models. The stepladder model has a numerical advantage in that it can be cast in the form of a tridiagonal matrix and be solved with very few computer operations and with minimal demand on CPU memory.[16] This model, as its name implies, involves a set of equispaced $\Delta\epsilon$ levels that extend below E_{01}, the threshold energy of the lowest of the two activation barriers in the cyclobutanone decomposition, and continues to well above E_{02}, the energy threshold for the upper channel. It is assumed that each collision with a heat bath molecular transfers energy either up or down with all perfectly elastic collisions excluded from consideration.[1] The total probability of an up-transfer of energy from a given level plus that for a down-transfer from the same level is, therefore, unity. The probability of transferring energy from level i to level $i + 1$ is proportional to the density of states at level $i + 1$ multiplied by the factor $\exp(-\Delta\epsilon/RT)$ while the probability of collisional energy transfer from level $i + 1$ to level i is proportional only to the density of states at level i. These conditions satisfy the criterion of microscopic reversibility and, since the density of states is calculable from known spectroscopic parameters, the entire energy transfer process can be described by the single parameter, $\Delta\epsilon$. The calculation of this quantity requires a value for the collision number which was computed from a tabulated set of Lennard-Jones parameters.[17]

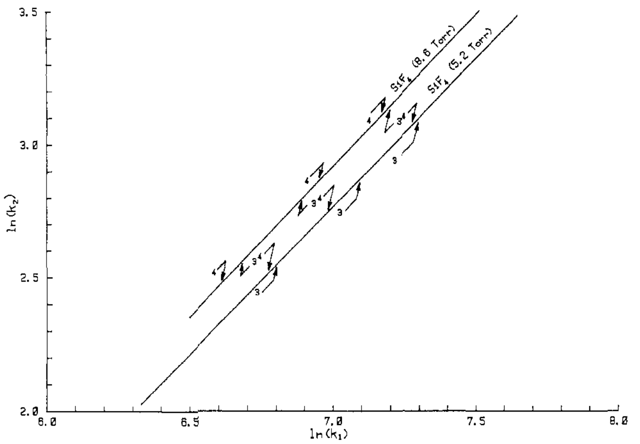

Figure 3. Comparison of the stepladder activation–deactivation model with cyclobutanone in SiF_4 data, using 3 and 4 kcal/mol steps.

The calculation of the macroscopic rate constant requires a computation of $k(E)$, the specific rate constant for molecules that are vibrationally excited to an energy E. The calculation further requires the choice of a transition-state structure which with the help of absolute reaction rate theory (ART) reproduces the high-pressure Arrhenius parameters in the temperature interval used for their experimental determination. The transition-state vibrational frequencies are then also applied to the calculation of the $k(E)$'s by means of standard RRKM procedures.[18,19] Table I gives values for E, $k_1(E)$, and $k_2(E)$ for the cyclobutanone decomposition. These $k(E)$'s are then incorporated in the stepladder activation–deactivation model and an integrated macroscopic rate constant is calculated for a particular pressure, temperature, and energy spacing $\Delta\epsilon$. The resulting rate constants that are computed over the experimental temperature range are plotted as in eq 3. That value of $\Delta\epsilon$ is sought which fits the experimental data best as shown in Figure 3. This is then identified as the average energy transferred during a collision between a heat bath molecule and cyclobutanone.

The computer code was designed to solve for the steady-state populations of cyclobutanone molecules at each energy step relative to that of the lowest step located below the threshold energy, E_{10}. When these populations are multiplied by the appropriate $k(E)$ and then integrated over all energies a relative rate constant is obtained for each of the two reaction channels. By performing an identical integration for a population whose distribution is in Boltzmann equilibrium at each step, a comparable relative rate constant at the high-pressure limit is obtained. When the ratio of these two relative rate constants is multiplied by the ART high-pressure rate constant determined previously, the absolute rate constant at the pressure and temperature of interest is the final result. The lowest step in the energy ladder was set at that point below E_{10} where the non-Boltzmann and Boltzmann populations are similar while the highest step above E_{20} was chosen at that level where the final values of the computed rate constant remained unchanged as higher steps were added.

Figure 3 shows least-squares comparative rate plots for the decomposition of cyclobutanone in a SiF_4 heat bath at pressures of 5.2 and 8.6 torr, respectively. The plotted numbers (3 and 4) designate the energy ladder step sizes in kcal/mol that were used to calculate ln (k_1) and ln (k_2) for these two experimental pressures. The arrows associated with each number point to the experimental line corresponding to the pressure (8.6 or 5.2 torr). It is seen that between 3 and 4 kcal/mol is the average energy transferred by a collision of an SiF_4 heat bath molecule with cyclobutanone. The slopes of lines through the 3's and 4's com-

---

(14) M. N. Das, F. Kern, T. D. Coyle, and W. D. Walters, *J. Am. Chem. Soc.*, **76**, 6271 (1954).

(15) A. T. Blades, *Can. J. Chem.*, **47**, 615 (1969).

(16) L. H. Thomas, "Elliptic Problems in Linear Difference Equations over a Network", Report of Watson Sci. Comp. Lab., Columbia University, New York, 1949.

(17) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids", 2nd ed, Wiley, London, 1963.

(18) W. Frost, "Theory of Unimolecular Reactions", Academic Press, New York, 1973.

(19) P. J. Robinson, and K. A. Holbrook, "Unimolecular Reactions", Wiley-Interscience, New York, 1972.

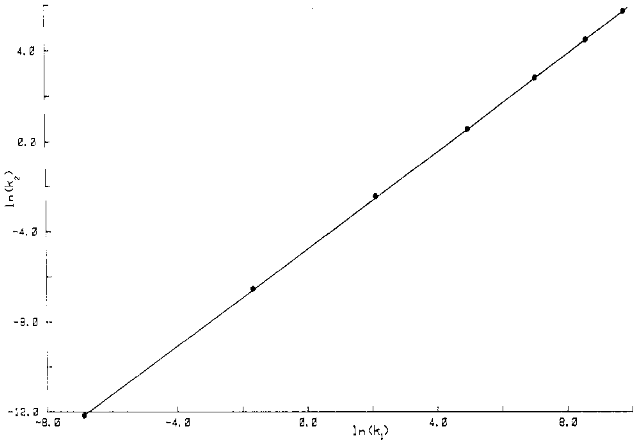

Figure 4. Comparative plot of the cyclobutanone decomposition in 10 torr of Ar between 650 and 1250 K as calculated with the stepladder model using 2 kcal/mol steps.

puted by the model are 1.1 in agreement with the experimental data. The computed best fits for the SF_6, SiF_4, He, and Ar heat baths were found to be 4, 3.5, 3, and 2 kcal/mol, respectively. Conservative estimates of the errors in the measurement of product composition, flow rates, and pressure lead to an uncertainty in these values of about 0.5 kcal/mol within the framework of the stepladder activation–deactivation model.

King et al.[8] studied the two-channel decomposition of chloroethane-*2-d* in which HCl and DCl are the products. Using a modification of the VLPP method, they obtained downward collisional energy transfer values of 1.7 kcal/mol for Kr and Ne and about 2.1 kcal/mol for He, in agreement with our observation that Ar transfers energy more efficiently than does He. They used a modified exponential energy transfer model, namely, $\exp(\Delta\epsilon^3)$, for the probability of collisionally transfering $\Delta\epsilon$ of vibrational energy. Such a stronger-than-exponential function is virtually indistinguishable from the simple stepladder model. Their results ($\Delta\epsilon \sim RT$) are in qualitative agreement with ours for the rare gas heat baths, despite the fact that the VLPP method was used to study a different unimolecular decomposition at much lower pressures where second-order kinetic behavior predominates.

The $\ln (k_1)$ vs. $\ln (k_2)$ plots for the cyclobutanone decomposition in the falloff region are observed to be linear with slopes equal to the ratio of activation energies obtained at the high-pressure limit. The intercepts ($\ln (A_2)-(E_2/E_1) \ln (A_1)$), on the other hand, are significantly lower than that calculated from the high-pressure preexponential factors. The stepladder model can be used to explore this decrease of the intercepts over a very wide temperature interval. Calculations for Ar as a heat bath at 10 torr in the 650–1250 K temperature range are shown in Figure 4. It is seen that the plot is linear with a slope characteristic of the high-pressure limit even though falloff of the upper channel is much greater than that of the lower one at the high end of the temperature range. It is of interest to pursue this simulation for the case where only one of the two reactions is in the falloff region. This may be artificially achieved by plotting the values of $\ln (k_2)$ obtained from the stepladder model calculations vs. the corresponding high-pressure $\ln (k_2)$'s that were obtained from absolute reaction rate theory in the 650–1250 K temperature range. The result is shown in Figure 5 which clearly exhibits a curvature with the slope approaching an upper limit of 1.0 at 650 K and gradually decreasing to a value considerably less than 1 as the temperature is increased. Such an effect has been confirmed by some preliminary studies of the reaction pair cyclohexene–cyclopropane in 10.0 torr of helium.[20] Under these conditions cyclopropane is well into the falloff region while cyclohexene is not. Over the 1000–1100 K temperature interval the experimental comparative plot was linear buth with a slope that was only about 60% of the high-pressure value.

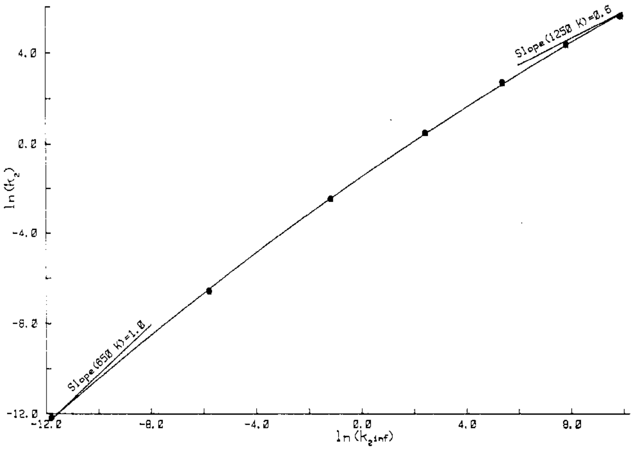

Figure 5. Comparative plot (with vs. without falloff) for channel 2 of the cyclobutanone decomposition in 10 torr of Ar between 650 and 1250 K as calculated with the stepladder model using 2 kcal/mol steps.

TABLE II: Calculated Arrhenius Parameters for the Two Channels of the Cyclobutanone Decomposition in the 1000–1100 K Temperature Range[a]

P/torr	$\Delta\epsilon$/ (kcal/mol)	$10^{-11}A_1$/ s	$10^{-10}A_2$/ s	E_1/ (kJ/mol)	E_2/ (kJ/mol)
5.2	2.0	2.0	0.6	167.2	176.2
8.6	2.0	4.2	1.6	171.7	181.0
5.2	3.0	6.5	2.3	174.5	182.8
8.6	3.0	13.2	5.7	178.9	187.9
5.2	4.0	14.3	6.8	179.4	189.0
8.6	4.0	27.8	17.2	183.6	194.3

[a] The limiting high-pressure values are $A_1 = 5.0 \times 10^{14}$ s^{-1}, $A_2 = 3.4 \times 10^{14}$ s^{-1}, $E_1 = 220$ kJ/mol, and $E_2 = 245$ kJ/mol.

Conclusions

It has been demonstrated that a comparative-rate method can be applied to unimolecular decompositions in the falloff region. With such a method, a set of high-temperature measurements of the kinetics of the unimolecular decomposition of cyclobutanone were made which together with their calculation by computer simulation has led to values for the average energy transferred between the cyclobutanone and heat bath molecules of varying complexity. There values were found to be a small fraction of the energy required to surmount the activation barrier, and even for SF_6, the most complex molecule studied, the average energy transferred did not exceed $2RT$. These results therefore indicate that weak collisions appear to dominate in such unimolecular decompositions and show that a general application of the strong collision assumption ($\Delta\epsilon >> RT$) to unimolecular processes cannot be justified.

Acknowledgment. Partial support for this investigation was provided by the AFOSR under Contract ISSA-83-00033.

Appendix

The kinetics of two simultaneously occurring decomposition reactions in contact with the same heat bath is given by

$$k_1 = (Z_1/\tau) \qquad k_2 = (Z_2/\tau) \tag{4}$$

where k_1 and k_2 are the rate constants whose Arrhenius temperature dependence is given by

$$k_x = A_x \exp(-E_x/RT) \tag{5}$$

The quantities Z_1 and Z_2 are product conversion factors which can be written in terms of the fractions (f_1 and f_2) of reactant converted to products in each of the reactions.

$$Z_1 = -\ln (1 - f_1) \qquad Z_2 = -\ln (1 - f_2) \tag{6a}$$

For the case of the decomposition of a single reactant into two

---

(20) M. D. Scheer, J. R. McNesby, and W. Braun, unpublished results.

separate channels, the quantitites become coupled and are given by

$$Z_1 = -(f_1/(f_1 + f_2)) \ln (1 - f_1 - f_2)$$
$$Z_2 = -(f_2/(f_1 + f_2)) \ln (1 - f_1 - f_2) \qquad (6b)$$

The common reaction time τ is equal to the duration of contact of the decomposing molecule with the heat bath while it is heated to temperatures that are high enough to lead to products. Substituting (5) and (6) into (4), eliminating T, and solving for τ yields

$$\tau = (Z_1/A_1)^{(E_2/(E_2-E_1))}(A_2/Z_2)^{(E_1/(E_2-E_1))} \qquad (7)$$

Thus, a knowledge of the fractional conversions for a given heat bath temperature history allows one to calculate a chemically effective reaction time provided the four Arrhenius parameters A_1, A_2, E_1, and E_2 are known.

These parameters were calculated in the 1000-1100 K temperature range for cyclobutanone in an SiF_4 heat bath at 5.2 and 8.6 torr by means of the stepladder model described under Results, section 2. The temperature history for a small volume of gas flowing through the reactor tube can be simulated by dividing the measured axial temperature profile into a large number of equally spaced isothermal zones. The Z's are then computed separately for each zone by means of eq 4 using the calculated Arrhenius parameters and the time taken for a zonal volume of gas to traverse a single zone length. Then f's calculated for each zone lead to total fractional conversions of the reactant molecules flowing through the entire tube length. From these, composite Z's are calculated so that, from eq 7, effective reaction times of 1.5 and 2.6 ms are obtained for pressures of 8.6 and 5.2 torr, respectively. When these times are multiplied by the known flow velocities, a value of about 5.8 cm is the average length obtained for that portion of the reactor tube in which the cyclobutanone is decomposing. An effective temperature of about 1020 K for this reaction length is readily calculated from the composite Z values by means of

$$T = ((E_2 - E_1)/R)/\ln ((Z_1A_2)/(A_1Z_2)) \qquad (8)$$

a formula resulting from a substitution of (5) and (6) into (4) and the eliminating of τ.

As stated above, the Arrhenius parameters were calculated for the cyclobutanone decomposition in the falloff region by means of the stepladder model. The results are given in Table II for the two pressures (5.2 and 8.6 torr) and $\Delta\epsilon$'s of 2, 3, and 4 kcal/mol. The calculated A's and E's all increase as the pressure and $\Delta\epsilon$'s (energy transfered per collision) are increased. They are all, however, much lower than the high-pressure limiting values. Despite these variations, the computed reaction times for the two pressures and the resulting effective reaction length remain unchanged. This arises from the fact that the ratio (E_2/E_1) is in all cases close to one. It can be readily shown, however, that, if the two reactions had very differrent activation energies, there would be a much greater sensitivity to the $\Delta\epsilon$ used in the simulation calculation and a laborious iteration procedure would be needed to obtain the $\Delta\epsilon$ that would best fit the experimental data. Thus for cyclobutanone, with an $(E_2/E_1) = 1.1$, an accurate effective reaction length may be obtained when only an approximate value of $\Delta\epsilon$ is used in the simulation calculation.

Registry No. He, 7440-59-7; Ar, 7440-37-1; SiF_4, 7783-61-1; SF_6, 2551-62-4; cyclobutanone, 1191-95-3.

A Study of the Collisional Activation of Cyclobutanone by the Transient Heating of SiF_4

Milton D. Scheer,* James R. NcNesby,[†] and Walter Braun

Center for Chemical Physics, National Bureau of Standards, Washington, D.C. 20234

(Received: June 7, 1983)

The unimolecular decomposition of cyclobutanone has been used to study the behavior of SiF_4 as a heat bath gas. Temperatures in the neighborhood of 1050 K were obtained by rapid flow through a heated tube and by the absorption of the pulsed infrared radiation emitted by a CO_2 TEA laser tuned to 1033 cm^{-1}. The effective reaction times of these two heating methods were approximately 1 ms and 100 μs, respectively. The two separate decomposition channels of cyclobutanone were studied by a comparative method that is insensitive to the nonuniform temperatures inherent in all transiet heating methods. It was shown that, between 5 and 30 torr, both channels are in the unimolecular falloff regime. Further at laser fluences greater than 0.5 J/cm^2, a third higher activation energy channel is opened with effective reaction times that are less than 10 μs. Times of this magnitude are too small for complete equipartition of the vibrational energy deposited in the heat bath and hence involves rapid v-v energy transfer to the cyclobutanone resulting in its excitation to near 300 kJ/mol and provides access to the third reaction channel.

Introduction

It has previously been shown[1] that the sensitization of unimolecular decompositions with heat bath molecules that absorb pulsed infrared laser radiation is characterized by longitudinal and transverse temperature inhomogeneities. These arise from the nature of the energy absorption process and the multimode nature of most infrared laser light sources. In addition to these complexities, there exists a number of other processes that tends to obscure our understanding of the chemistry that takes place in such systems. During the laser pulse, the absorbed radiation excites the heat bath molecules to high vibrational levels by means of a multiphoton process. Collisions then tend to equipartition this deposited energy and at the same time begin to activate the reactant molecules that are usually present at low levels of abundance. The times for equipartition and reactant activation are important parameters for characterizing the chemistry of these systems since decomposition accompanies activation at a rate usually described by RRKM theory. Equipartition is also accompanied by a pressure increase in the irradiated volume so that the cooling due to the subsequent expansion is followed by further cooling due to the diffusion of thermal energy to the vessel walls under highly turbulent conditions. This hierarchy of cooling processes tends to quench the decomposition and hence set a limit on the reaction time. Finally, it must also be recognized that complete Boltzmann equilibration of the high vibrational levels of the reactant molecules is inhibited by their depletion as a consequence of the decomposition process itself. It is our intention to deal with this complex network of effects in a semiquantitative way in order to provide a guide for the understanding of such

---

[†] Chemistry Department, University of Maryland, College Park, MD 20742.

(1) Starov, V. Selamoglu, N.; Steel, C. *J. Am. Chem. Soc.* **1981**, *103*, 7276.

0022-3654/84/2088-1850$01.50/0 © 1984 American Chemical Society